

1

2,718,516

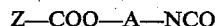
ISOCYANATO ESTERS OF ACRYLIC, METHACRYLIC, AND CROTONIC ACIDS

Newman M. Bortnick, Orelan, Pa., assignor to Rohm & Haas Company, Philadelphia, Pa., a corporation of Delaware

No Drawing. Application November 8, 1952,
Serial No. 319,603

12 Claims. (Cl. 260—86.1)

This invention relates to polymerizable isocyanato esters of acrylic acid, methacrylic acid, α -chloroacrylic acid and crotonic acid, all of which esters have the general formula



in which A represents an alkylene group, C_nH_{2n} , in which n is an integer having a value of 2 to 14 inclusive, and in which Z represents the following groups: $CH_2=CH-$; $CH_2=C(CH_3)-$; $CH_2=C(Cl)-$; and $CH_3CH=CH-$. This invention also relates to the polymers of these isocyanato esters and to the copolymers of these esters and other copolymerizable compounds which contain at least one vinylidene group, $CH_2=C<$.

Esters having the above general formula undergo addition polymerization, particularly in the presence of a free-radical catalyst, and thereby form soluble, thermoplastic, resinous polymers of high molecular weight which contain a plurality of reactive isocyanato groups. The isocyanato groups in the polymers can, in turn, react with compounds containing, for example, amino, hydroxyl, mercapto or carboxyl groups, all of which groups contain reactive hydrogen atoms. In this way a wide variety of substituent groups can be added to the resinous molecules which increase the uses of the polymers. Furthermore, the isocyanato groups in the polymers are reactive with the hydroxyl or amino groups of carbohydrates, including cellulosic compounds, and of proteinaceous materials such as proteins per se and wool. Thus, the isocyanato polyesters serve to cross-link the molecules and greatly alter the physical and chemical properties of the carbohydrates and proteinaceous materials. Wool is readily altered and is rendered very resistant to shrinkage by treatment with the polymeric isocyanato esters of this invention since a true chemical reaction, involving the isocyanato groups, takes place between the polymer and the wool, as a result of which the wool and the polymer become chemically joined.

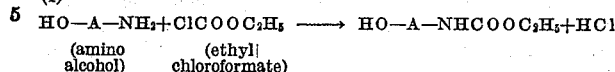
Not only do the polymeric isocyanato esters serve as cross-linking agents for other materials containing a plurality of reactive hydrogen atoms, but they can, themselves, be cross-linked and thus rendered substantially insoluble and infusible. For this purpose, compounds containing two or more active hydrogen atoms, such as polyamines, polyhydric alcohols, amino alcohols and polycarboxylic acids are employed. Examples of these include ethylenediamine, diethylenetriamine, triethylenetetramine, ethylene glycol, polyethylene glycols such as triethylene glycol, glycerol, pentaerythritol, sorbitol, mannito, oxalic acid, adipic acid, ethanolamine, diethanolamine and propanolamine. The polymeric isocyanato esters also react with the free hydroxyl or carboxyl groups of alkyl resins thus giving rise to new cross-linked products.

The monomeric isocyanato esters of this invention can be made by a variety of ways, but the method which has proven to be eminently suitable involves the procedural steps which are represented by the following general

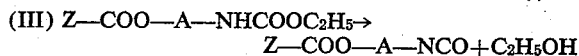
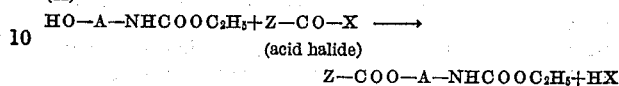
2

equations in which the various characters have the significance described above and X is a halogen atom—preferably a chlorine atom.

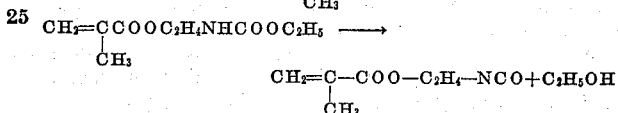
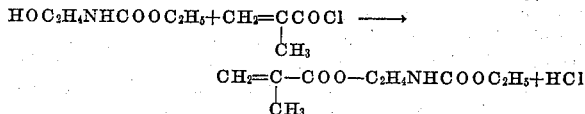
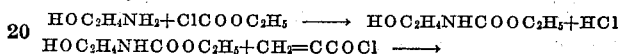
(I)



(II)



15 This process may be more readily understood from the following equations which show the preparation of one particular isocyanato ester, namely β -isocyanatoethyl methacrylate:

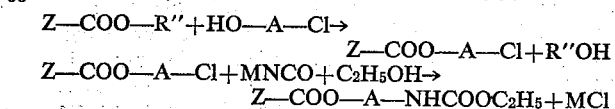


30 Step I of the process is best carried out by adding the chloroformate slowly to a solution of the amino alcohol in a solvent such as benzene, toluene, chloroform, methanol or ethanol. An HCl-acceptor, such as sodium hydroxide, potassium carbonate, pyridine, triethylamine or the like, should be present and, to assure best results, the temperature should not rise above 80° C.—preferably not above 60° C.—during the addition of the chloroformate. The mixture is then heated, preferably at refluxing temperature, until the reaction is substantially complete, after which the reaction product is freed of salt and solvent and is used as such or is purified by distillation.

In the second step of the process, represented by Equation II, it is most desirable to employ an HCl-acceptor. Here, however, the choice is more limited than in the step of Equation I because various complications may occur. Hence it is strongly recommended that acrylonitrile be employed in order to take up the liberated HCl and also to serve as a solvent for the reaction mixture. When compared with other materials, such as alkali metal compounds, pyridine and amines, acrylonitrile is surprisingly superior in this step.

The hydroxycarbamate, prepared in step I, is dissolved in acrylonitrile and the acrylyl chloride, $Z-\text{COCl}$, is added. The mixture is heated to above 80° C. at which point an exothermic reaction begins. After the exothermic reaction diminishes, the mixture is heated for a period of a few hours at about 80° C. after which it is stripped of acrylonitrile and β -chloropropionitrile. The urethano ester is purified, preferably by distillation under reduced pressure or can be used as such in the next step.

Another procedure for making the intermediate urethano ester involves the reaction of an ester, $Z-\text{COO}-\text{alkyl}$ and a chloroalcohol according to these equations in which R'' is a lower alkyl group and MNCO is a metallic isocyanate such as KNCO or NaNCO :



70 An example of this procedure is given later. Here the more readily available esters are employed instead of the acid halides. The process is, however, restricted for the